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Generation and reactions of thiocarbonyl *S*-(2,2,2-trifluoroethanides). Synthesis of trifluoromethylated 1,3-dithiolanes, thiiranes and alkenes

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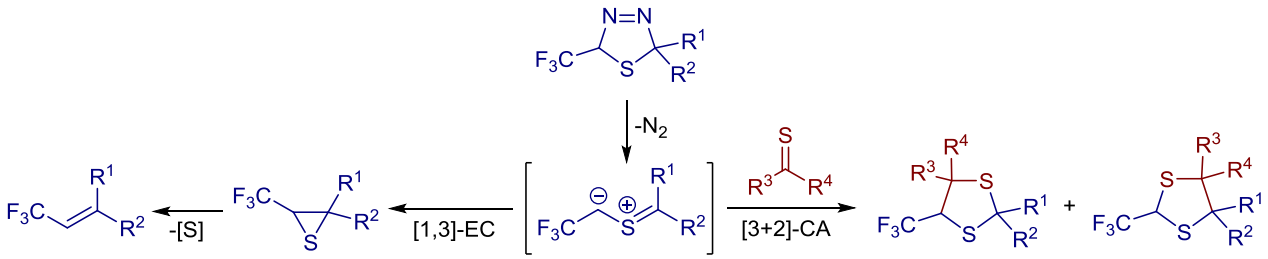
Abstract

The '*in situ*' generated 1,1,1-trifluorodiazoethane reacts with thioketones as C=S dipolarophiles in a two-phase system (DCM/H_2O) at room temperature to yield trifluoromethylated 2,5-dihydro-1,3,4-thiadiazoles. Whereas stable crystalline products were obtained with cyclobutanethiones, the reaction with aromatic and heteroaromatic thioketones occured with spontaneous elimination of nitrogen. The formation of sterically crowded 4,4,5,5-tetrahetaryl-1,3-dithiolanes indicates that thiocarbonyl *S*-methanides are formed immediately and entered formal [3+2]-cycloaddition as diradical species with the starting thioketone. A protocol for the preparation of 3,3,3-trifluoropropene derivatives starting from corresponding thioketones and 1,1,1-trifluorodiazoethane is also presented.

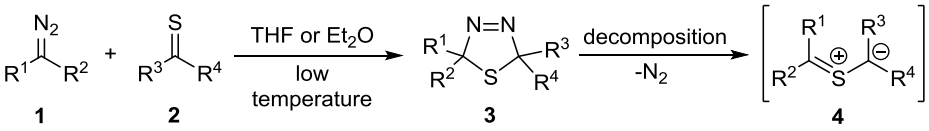
Keywords: [3+2]-Cycloadditions, thioketones, diazo compounds, fluorinated heterocycles, desulfurization reaction

Graphical abstract



1. Introduction

Thiocarbonyl *S*-methanides **4** belong to the class of so-called sulfur-centered allyl-type [1,3]-dipoles, which can be easily generated by thermal cycloreversion of the corresponding 2,5-dihydro-1,3,4-thiadiazoles **3** [1]. The precursors **3** are available *via* [3+2]-cycloaddition reactions of diazo compounds **1** with thioketones **2**, and diverse thioketones were shown to be superior reaction partners. Typically, the reactions with diazomethane occur already at low temperature yielding the required cycloadducts in a regioselective manner and almost quantitative yields (Scheme 1). Different mechanisms of [3+2]-cycloadditions with application of thiocarbonyl *S*-methanides **4** as the *in situ* generated reactive 1,3-dipoles are considered, *i.e.* concerted [2a], stepwise reactions via zwitterionic [2b,c] or diradical [2d] intermediates.



Scheme 1. Generation of thiocarbonyl *S*-methanides.

The stability of 1,3,4-thiadiazoles of type **3** depends strongly on the type of the substituents R^1–R^4. For example, in the case of diazomethane **1** (R^1 = R^2 = H), cycloadducts **3** obtained with aryl thioketones **2** (R^3 = R^4 = Ar) decompose at –40 °C, whereas cycloaliphatic thioketones **2a** and **2b** gave the corresponding products **3** as fairly stable compounds, which release nitrogen only upon heating to *ca.* 45 °C.

The generation of thiocarbonyl *S*-methanides **4** in the presence of suitable dipolarophiles leads to the [3+2]-cycloadducts, and thioketones were found to react as 'superdipolarophilic' reagents to give 1,3-dithiolanes with variable regioselectivity. On the other hand, in the absence of a trapping agent, they undergo [1,3]-dipolar electrocyclization leading to thiiranes or dimerize to yield, in most cases, the sterically more crowded 1,4-dithianes [3].

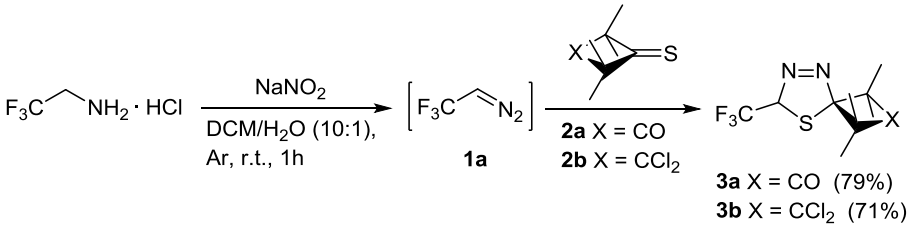
Thiocarbonyl *S*-methanides which contain fluorine atoms in their structure are scarcely reported in the literature. In our earlier publication however, reactions of diazomethane with fluorinated benzyl pentanedithioates leading to dimers of the intermediate thiocarbonyl ylides were described [4]. Furthermore, hexafluorothioacetone was reacted with diphenyldiazomethane, and after spontaneous elimination of nitrogen, 2,2-diphenyl-3,3-bis(trifluoromethyl)thiirane was obtained [5]. Finally, hexafluorothioacetone and 2-diazohexafluoropropane formed the stable 2,2,5,5-tetrakis(trifluoromethyl)-2,5-dihydro-1,3,4-thiadiazole [6].

1,1,1-Trifluorodiazoethane (**1a**) is easily available *via* direct diazotization of commercially available 2,2,2-trifluoroethylamine hydrochloride and recently has extensively been explored as a versatile fluorine-containing organic building block. The [3+2]-cycloaddition reactions with **1a** and dipolarophiles such as metal acetylides [7], alkynes [8], alkenes [9], and the C≡P group [10] were reported in recent years. Cyclopropanations of alkenes were performed with **1a** *via* sequencial cycloaddition/elimination reaction [11]. However, **1a** has not yet been used in cycloaddition reactions with thioketones (C=S dipolarophiles).

Due to our ongoing interest in the exploration of thioketones as useful building blocks in the synthesis of diverse fluoroalkylated *S*-heterocycles [12], we performed a study aimed at the examination of their reactions with 1,1,1-trifluorodiazoethane (**1a**).

2. Results and discussion

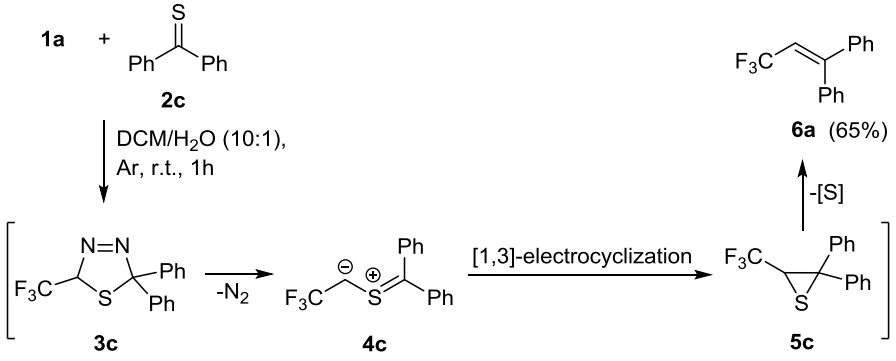
Two thioketones, the cycloaliphatic 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**2a**) and aromatic thiobenzophenone (**2c**) were selected for examination of the reactivity of **1a** towards C=S dipolarophiles. The reactions with **2a** and **2c** were performed at room temperature with the '*in situ*' generated **1a** (Scheme 2). The characteristic colour of thioketones disappeared within *ca*. 1 h, and after typical aqueous workup, the crude products were analyzed by ^{1}H NMR spectroscopy. The solid product obtained from **2a** showed four signals for methyl groups and a characteristic quartet at 6.71 ppm ($^{3}J_{H,F}$ = 6.6 Hz). These data suggested that the expected 2,5-dihydro-1,3,4-thiadiazole **3a** was formed as the sole product. The ^{13}C NMR spectrum confirmed this structure by the presence of two signals at 97.6 ppm (q, $^{2}J_{C,F}$ = 28.9 Hz) and 117.2 ppm (s), which were attributed to C(7) and C(4), respectively. The molecular mass for $C_{10}H_{13}F_3N_2OS$ was confirmed by ESI-MS and corresponded to the results of the elemental analysis. In analogy to the cycloadduct obtained from **2a** and diazoethane [13], **3a** was stable at room temperature.



Scheme 2. Generation of 1,1,1-trifluorodiazoethane (**1a**) and its [3+2]-cycloaddition with thioketones **2a**,**b**.

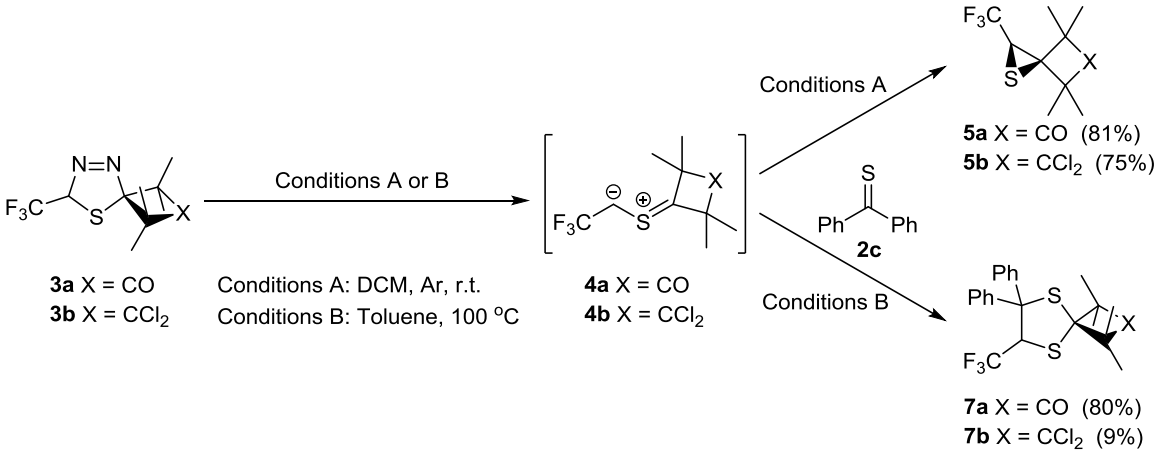
In addition to **2a**, 3,3-dichloro-2,2,4,4-tetramethylcyclobutanethione (**2b**) was treated with **1a** under analogous conditions (two-phase system DCM/H_2O, Ar, room temperature, *ca*. 1 h) and the only observed product was the corresponding 2,5-dihydro-1,3,4-thiadiazole **3b** (Scheme 2). Also in that case, no decomposition was observed at room temperature.

The experiment with **2c** led to an oily product, which in the ^{1}H NMR spectrum along with signals of the phenyl groups displayed a single quartet at 6.17 ppm ($^{3}J_{H,F}$ = 8.3 Hz). In the ^{13}C NMR spectrum, two signals located at 115.5 ppm (q, $^{2}J_{C,F}$ = 33.8 Hz) and 152.5 ppm (q, $^{3}J_{C,F}$ = 5.6 Hz), together with the typical quartet for the trifluoromethyl group (CF_3) at 123.1 ppm (q, $^{1}J_{C,F}$ = 270.6 Hz), suggested the structure of the alkene **6a** [14] (Scheme 3). This assumption was also confirmed by MS measurement. The observed instability of the initially formed cycloadduct **3c** is in line with the reported behavior of the analogous product obtained with diazomethane [15]. Apparently, the presence of the electron-withdrawing trifluoromethyl group accelerates the extrusion of the sulfur atom.



Scheme 3. Formation of alkene **6a** in the reaction of **1a** with thiobenzophenone (**2c**).

The isolated cycloadducts **3a** and **3b** were used as precursors of fluorinated thiocarbonyl *S*-methanides **4a**,**b** (Scheme 4). In the first series of experiments, their solutions in dichloromethane were stirred at room temperature overnight. The isolated products showed similar sets of signals in the ^{1}H NMR spectra with four singlets for Me groups and a quartet attributed to a CH–CF_3 group. The ^{13}C NMR spectra revealed signals at 64.0 and 65.3 ppm, respectively. The comparison with structurally similar spirothiiranes [13] allowed to attribute them the structures of thiirane derivatives **5a** and **5b**. In both cases, the molecular masses were confirmed by mass spectrometry.



Scheme 4. [1,3]-Dipolar electrocyclization and [3+2]-cycloaddition of thiocarbonyl ylides **4a** and **4b** with thiobenzophenone (**2c**).

The thermal decomposition of the isolated 2,5-dihydro-1,3,4-thiadiazoles **3a,b** in toluene at 100 °C in the presence of equimolar amounts of aromatic thioketones, *i.e.* thiobenzophenone (**2c**), di(thiophen-2-yl) thioketone (**2e**) and di(selenophen-2-yl) thioketone (**2f**), was aimed at trapping of the initially formed fluorinated thiocarbonyl ylides **4** with C=S dipolarophiles. In a typical experiment with **3a** and **2c**, the reaction was complete after 24 h, and subsequent chromatographic workup led to a single crystalline product, which was identified as the expected 1,3-dithiolane **7a** (Scheme 4). The structure of this regioisomer was elucidated on the basis of its ^{13}C NMR spectrum. Two quartets at 125.0 and 61.2 ppm are characteristic for the CF_3–CH unit. The chemical shift of the high-field signal corresponds with the range of values reported for analogous, sterically less crowded regioisomers [3]. Finally, the structure **7a** was unambigously proved by the X-ray structure investigation [16] (Figure 1).

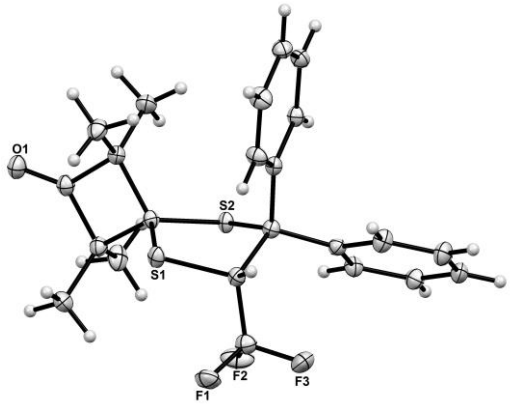
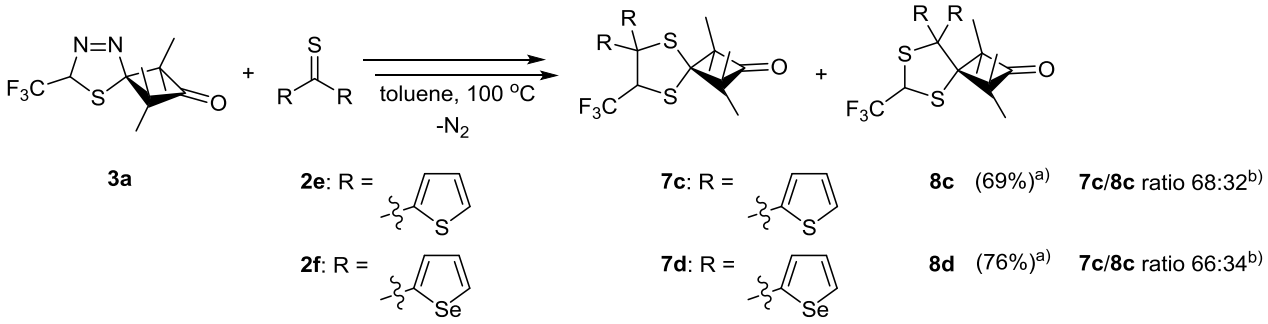


Figure. 1. ORTEP plot of the molecular structure of the 1,3-dithiolane **7a** [17]. Displacement ellipsoids are drawn at the 50% probability level.

An analogous result was obtained in the reaction of **3b** with thiobenzophenone (**2c**). However, in that case, the 1,3-dithiolane **7b** was isolated as the sole product in only 9% yield (Scheme 4).

Hetaryl-containing thioketones **2e** and **2f** used in reactions with thiocarbonyl *S*-methanides tend to form the sterically more crowded 1,3-dithiolanes as major or exclusive products [18]. Both thioketones were used for the reaction with **3a**, performed analogously to the experiment with **2c**. In both reactions, two regioisomeric 1,3-dithiolanes of type of **7** and **8** were formed in a ratio of *ca.* 2:1 (based on the ^{1}H NMR spectra) (Scheme 5). In the ^{13}C NMR spectra of the isolated mixtures, the sterically less crowded regioisomers **7c** and **7d** were identified by the signal for CF_3–CH units found at 64.3 ppm (q, $^{2}J_{C,F}$ = 26.7 Hz) and 64.3 ppm (q, $^{2}J_{C,F}$ = 26.7 Hz), respectively, as the major components. The corresponding signals for the minor regioisomers **8c,d** were found at 48.1 ppm (q, $^{2}J_{C,F}$ = 31.2 Hz) and 48.7 ppm (q, $^{2}J_{C,F}$ = 32.7 Hz), respectively. The different outcome of the investigated reactions with **2c** and **2e**,**f** demonstrates once more that the reaction mechanisms of the formed [3+2]-cycloadditions follow different pathways [18]. Whereas the regioselective formation of **7a** is in accordance with a concerted mechanism of the cycloaddition, the mixtures of regioisomeric cycloadducts **7c/8c** and **7d/8d** result from the competitive stepwise diradical pathway, which allows the formation of the sterically more crowded isomers **8c** and **8d**.

The same tendency, observed in the experiments with fluorinated thiocarbonyl *S*-methanide **4a**, was reported earlier for the corresponding *S*-methanide [18]. The explanation of this type of regioselectivity is based on the assumption of a diradical mechanism and stabilization of the radical centre on the ‘benzhydryl’ C-atom in the intermediate diradical. This regioselectivity, which results from the diradical nature of the postulated intermediate of the final 1,3-dithiolane, was also confirmed by a computational study [19]. The presence of the trifluoromethyl group in the intermediate thiocarbonyl *S*-ethanide reduces the tendency for the stepwise diradical formation of 1,3-dithiolanes.



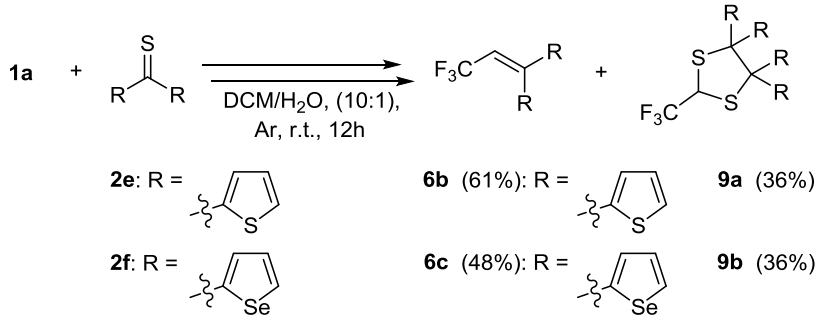
Scheme 5. Formation of regioisomeric 1,3-dithiolanes **7** and **8**.

a) For both regioisomers **7** and **8**.

b) Based on the ^{1}H-NMR spectrum.

In a recent publication we have reported reactions of diazomethane with hetaryl thioketones, which, even at very low temperature, occurred with spontanous elimination of a nitrogen molecule [20]. In these reactions, the sterically more crowded 4,4,5,5-tetrasubstituted 1,3-dithiolanes were formed side by side with dimers of the intermediate thiocarbonyl ylides. These results were rationalized by stepwise diradical mechanisms.

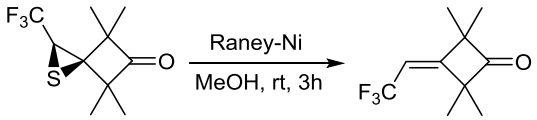
The hetaryl thioketones **2e**,**f** were also examined in reactions with 1,1,1-trifluorodiazoethane (**1a**) in the two-phase system (DCM/H_2O) at room temperature, in analogy to the experiment with thiobenzophenone (**2b**, Scheme 3). In both reactions, two products were formed, which were separated using standard column chromatography. The less polar fractions, obtained as oils, were easily identified as the trifluoropropenes **6b** and **6c**, respectively, on the basis of their ^{1}H and ^{13}C NMR spectra (Scheme 6). The more polar products, isolated as solids, revealed in the ^{13}C NMR spectra two signals attributed to sp^3 carbon atoms located at 50.5/50.8 ppm (q, $^{2}J_{C,F}$ = 33.0, 32.9 Hz) and 74.7/78.3 ppm (s). In the ^{1}H NMR spectra, the characteristic signals for the CH-CF_3 groups were found at 5.14/5.16 ppm (q, $^{3}J_{H,F}$ = 6.8, 7.1 Hz). In each case, the ratio of integrals of this H-atom to the entire group of hetaryl H-atoms was 1:12. These data prove that thioketones **2e**,**f** and **1a** reacted in a ratio of 2:1, and the sterically more crowded 1,3-dithiolanes **9a**,**b** are the products (Scheme 6). The observed regioselectivity confirms the explanation that heteroaromatic substituents promote the formation of diradical intermediates in the course of formal [3+2]-cycloadditions leading to 1,3-dithiolanes [15,18,20].



Scheme 6. Reaction of **1a** with dihetaryl-substituted thioketones **2e**,**f**.

Fluorinated alkenes are of current interest and the development of new methods for their preparation is a challenging task for modern organic chemistry [14,21]. Some thiiranes described in this study underwent

spontanous desulfurization and the corresponding 3,3,3-trifluoropropenes **6a**–**6c** were formed as final products. The stable thiirane **5a** was used for desulfurization with Raney-Ni in methanol at room temperature. The expected alkene **6d** was isolated in 68% yield (Scheme 7).



5a **6d** (68%)

Scheme 7. Desulfurization reaction of **5a** with application of Raney-Ni.

3. Conclusions

The '*in situ*' generated 1,1,1-trifluorodiazoethane is less reactive in [3+2]-cycloaddition reactions with thioketones than the parent non-fluorinated diazoethane. For that reason, its reactions with both cycloaliphatic and aromatic thioketones were carried out at room temperature. Under these conditions, stable 2,5-dihydro-1,3,4-thiadiazoles were obtained only with cyclobutanethiones, which were subsequently used as precursors of CF_3-containing thiocarbonyl *S*-methanides. The reaction with aromatic and heteroaromatic thioketones occurred with immediate evolution of nitrogen, and the reactive intermediate thiocarbonyl *S*-methanides undergo competitively [1,3]-dipolar electrocyclization to give the corresponding thiiranes or are trapped by the starting thioketone to yield the sterically more crowded 1,3-dithiolanes. The latter course was observed in reactions with hetaryl thioketones, indicating the immediate formation of the thiocarbonyl ylides as diradical species. The presented protocol for the preparation of 3,3,3-trifluoropropene derivatives *via* two-fold extrusion reaction offers an alternative approach to these attractive fluorinated building blocks.

4. Experimental

4.1. General information

Solvents and chemicals were purchased and used as received without further purification. 2,2,2-Trifluoroethylamine hydrochloride was purchased from FluoroChem. Sodium nitrite was purchased from Avantor. Cycloaliphatic (**2a**,**b**), aryl (**2c**), and hetaryl (**2e**,**f**) thioketones were prepared following the literature procedures by thionation of the corresponding ketones using Lawesson's reagent or diphosphorus pentasulfide (P_2S_5) [22]. The obtained products were purified by standard column chromatography on silica gel (230–400 mesh, Merck) or FLASH column chromatography using a Grace Reveleris X2 apparatus with UV–Vis and ELSD detection (commercially available 12 g or 24 g SiO_2 columns, pressure 20–25 psi, solvent flow rate 25–28 ml/min). Petroleum ether with increasing amounts of dichloromethane (DCM) was used as eluent. Unless stated otherwise, yields refer to analytically pure samples. NMR spectra were recorded with a Bruker Avance III 600 MHz (^{1}H NMR [600MHz]; ^{13}C NMR [151 MHz]) or with a Varian Gemini 2000BB 200 MHz (^{19}F NMR [188 MHz]) instrument. Chemical shifts are reported in ppm relative to solvent residual peaks (^{1}H NMR: δ = 7.26 ppm [$CDCl_3$]; ^{13}C NMR: δ = 77.0 ppm [$CDCl_3$]). For detailed peak assignments

2D (HMQC) spectra were measured. IR spectra were measured with a FTIR NEXUS spectrometer (as film or KBr pellets). Elemental analyses were obtained with a Vario EL III (Elementar Analysensysteme GmbH) instrument. High-resolution MS spectra were performed with a GCT Premier Waters instrument. Melting points (mp) were determined in capillaries with a Stuart SMP30 apparatus. Single crystal X-ray data were collected with a Bruker SMART APEX II CCD diffractometer (Cu Kα radiation, λ = 1.54178 Å, 30W Incoatec Microfocus Source IμS with Montel optics); the structure solution and refinement was performed using SHELXS-97 [16a] and SHELXL-2014 [16b]. Crystallographic data have been deposited at the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC–1525187 [17].

*4.2. Synthesis of the trifluoromethylated 2,5-dihydro-1,3,4-thiadiazoles **3a**,**b***

To a DCM/H_2O (10 ml, v/v: 10:1) solution of the corresponding thioketone **2a**,**b** (1.0 mmol) and sodium nitrite (207 mg, 3.0 mmol), solid 2,2,2-trifluoroethylamine hydrochloride (271 mg, 2.0 mmol) was added at room temperature, under inert atmosphere (Ar). The reaction mixture was vigorously stirred at this temperature until the color of the starting thioketone faded (typically up to 60 min). After this time, water (15 ml) was added and the product was extracted using DCM (3x10 ml). The organic layers were combined, dried over anhydrous Na_2SO_4, and the solvent was removed on rotary evaporator (important: cold water bath!). The resulting oil was crystallized from petroleum ether or hexane in dry ice.

*4.2.1. 1,1,3,3-Tetramethyl-7-(trifluoromethyl)-8-thia-5,6-diazaspiro[3.4]oct-5-en-2-one (**3a**).* Yield: 210 mg (79%); pale-pink solid, mp 49–50 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.20 (s, 3H, Me), 1.32 (s, 3H, Me), 1.33 (s, 3H, Me), 1.36 (s, 3H, Me), 6.71 (q, $^3J_{H,F}$ = 6.6 Hz, 1H, HC(5)); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 18.5 (s, Me), 19.0 (s, Me), 23.7 (s, Me), 24.0 (s, Me), 66.9 (s, $C(Me)_2$), 68.3 (s, $C(Me)_2$), 97.6 (q, $^2J_{C,F}$ = 28.9 Hz, C(5)), 117.2 (s, spiro-C), 122.1 (q, $^1J_{C,F}$ = 279.8 Hz, CF_3), 216.2 (s, C=O); ^{19}F NMR ($CDCl_3$, 188 MHz): δ –71.58 (d, $^3J_{H,F}$ = 6.6 Hz, CF_3); IR (KBr): ν 2965–2868 (C–H), 1774 (C=O), 1575, 1457, 1318, 1261, 1173, 1128–1089 (CF_3), 1021, 929, 865 cm^{-1}; ESI-MS: *m*/*z* 265.3 (100, $[M–H]^–$); elemental analysis calcd. (%) for $C_{10}H_{13}F_3N_2OS$ (266.28): C 45.11, H 4.92, N 10.52, S 12.04; found: C 45.04, H 5.15, N 10.31, S 12.28.

*4.2.2. 2,2-Dichloro-1,1,3,3-tetramethyl-7-(trifluoromethyl)-8-thia-5,6-diazaspiro[3.4]oct-5-ene (**3b**).* Yield: 228 mg (71%); pale-pink solid, mp 43–45 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.25 (s, 3H, Me), 1.31 (s, 3H, Me), 1.50 (s, 3H, Me), 1.52 (s, 3H, Me), 6.53 (q, $^3J_{H,F}$ = 6.6 Hz, 1H, HC(5)); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 21.7 (s, Me), 22.1 (s, Me), 27.6 (s, Me), 27.8 (s, Me), 58.3 (s, $C(Me)_2$), 59.2 (s, $C(Me)_2$), 96.9 (q, $^2J_{C,F}$ = 28.9 Hz, C(5)), 98.8 (s, spiro-C), 121.1 (s, CCl_2), 122.1 (q, $^1J_{C,F}$ = 279.8 Hz, CF_3); ^{19}F NMR ($CDCl_3$, 188 MHz): δ –71.32 (d, $^3J_{H,F}$ = 6.6 Hz, CF_3); IR (KBr): ν 3040–2840 (C–H), 1464, 1388, 1266, 1197, 1183–1106 (CF_3), 1040, 927, 817 cm^{-1}; ESI-MS: *m*/*z* 319.3, 321.2 (70, 40 $[M–H]^–$); elemental analysis calcd. (%) for $C_{10}H_{13}Cl_2F_3N_2S$ (321.18): C 37.40, H 4.08, N 8.72, S 9.98; found: C 37.41, H 4.08, N 8.69, S 9.84.

*4.3. Synthesis of the trifluoromethylated thiiranes **5a**,**b***

To a mixture of DCM/H_2O (10 ml, v/v: 10:1), the appropriate thioketone **2a**,**b** (1.0 mmol), sodium nitrite (207 mg, 3.0 mmol), and solid 2,2,2-trifluoroethylamine hydrochloride (271 mg, 2.0 mmol) were added at room temperature under Ar atmosphere. The mixture was vigorously stirred at this temperature until the color of the starting thioketone faded, then the mixture was left at room temperature overnight. After this time, water (15 ml) was added and the product was extracted using DCM (3x10 ml). The organic layers were combined, dried over anhydrous Na_2SO_4, and the solvent was removed *in vacuo*. The resulting oil was purified by standard column chromatography (SiO_2, mixture of petroleum ether/DCM, in gradient) or FLASH column chromatography to obtain analytically pure products.

*4.3.1. 4,4,6,6-Tetramethyl-1-(trifluoromethyl)-2-thiaspiro[2.3]hexan-5-one (**5a**).* Yield: 193 mg (81%); colorless oil; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.08 (s, 3H, Me), 1.24 (s, 3H, Me), 1.33 (s, 3H, Me), 1.38 (brd, $^6J_{H,F}$ = 1.4 Hz, 3H, Me), 3.48 (q, $^3J_{H,F}$ = 5.5 Hz, 1H, HC(2)); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 21.6 (q, $^5J_{C-F}$ = 3.5 Hz, Me), 22.2 (s, Me), 23.0 (s, Me), 23.9 (s, Me), 37.2 (q, $^2J_{C,F}$ = 40.3 Hz, C(2)), 61.8 (s, $C(Me)_2$), 62.0 (s, $C(Me)_2$), 64.0 (brd, $^3J_{C,F}$ = 0.9 Hz, spiro-C), 124.4 (q, $^1J_{C,F}$ = 273.6 Hz, CF_3), 217.4 (s, C=O); ^{19}F NMR ($CDCl_3$, 188 MHz): δ –65.31 (d, $^3J_{H,F}$ = 5.5 Hz, CF_3); IR (film): ν 2977–2866 (C–H), 1831, 1790 (C=O), 1546, 1458, 1385, 1271, 1220–1131 (CF_3), 1107, 916, 878, 706 cm^{-1}; HRMS (EI): *m/z* calcd. for $C_{10}H_{14}F_3OS$ ($[M+H]^+$): 239.2709, found: 238.2715 [100].

*4.3.2. 5,5-Dichloro-4,4,6,6-tetramethyl-1-(trifluoromethyl)-2-thiaspiro[2.3]hexane (**5b**).* Yield: 220 mg (75%); colorless oil; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.17 (s, 3H, Me), 1.35 (s, 3H, Me), 1.53 (s, 3H, Me), 1.59 (brs, 3H, Me), 3.20 (q, $^3J_{H,F}$ = 6.1 Hz, 1H, HC(2)); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 25.2 (q, $^5J_{C,F}$ = 2.9 Hz, Me), 26.2 (s, Me), 26.5 (s, Me), 27.7 (s, Me), 35.8 (q, $^2J_{C,F}$ = 40.4 Hz, C(2)), 53.7 (s, $C(Me)_2$), 54.8 (s, $C(Me)_2$), 65.3 (brs, spiro-C), 99.5 (s, $C(Cl)_2$), 124.4 (q, $^1J_{C,F}$ = 273.7 Hz, CF_3); ^{19}F NMR ($CDCl_3$, 188 MHz): δ –64.82 (d, $^3J_{H,F}$ = 6.0 Hz, CF_3); IR (film): ν 2980–2826 (C–H), 1620, 1460, 1364, 1291–1236 (CF_3), 1122, 899, 766, 685 cm^{-1}; HRMS (EI): *m/z* calcd. for $C_{10}H_{13}Cl_2F_3S$ ($[M+H]^+$): 293.0140, found: 293.0133[100], 295.0103 [70].

*4.4. Synthesis of the trifluoromethyl-substituted alkenes **6a** and **6d***

*4.4.1. 3,3,3-Trifluoro-1,1-diphenylprop-1-ene (**6a**).* To a DCM/H_2O (10 ml, v/v: 10:1) solution of thiobenzophenone (**2c**, 1.0 mmol) and sodium nitrite (207 mg, 3.0 mmol), solid 2,2,2-trifluoroethylamine hydrochloride (271 mg, 2.0 mmol) was added at room temperature under inert atmosphere (Ar). The mixture was stirred at this temperature until the color of **2c** disappeared (60 min). Then, water (15 ml) was added and the product was extracted using DCM (3x10 ml). The organic layers were combined, dried over anhydrous Na_2SO_4, and the solvent was removed *in vacuo*. The resulting oil was purified by column chromatography to give **6a**. Yield: 161 mg (65%); colorless oil. All spectral data are consistent with those from ref. [14]. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 6.17 (q, $^3J_{H,F}$ = 8.3 Hz, 1H, HC(1)), 7.28–7.30 (m, 4CH, Ph), 7.35–7.40 (m, 3CH, Ph), 7.43–7.44 (m, 3CH, Ph); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 115.5 (q, $^2J_{C,F}$ = 33.8 Hz, C(1)), 123.1 (q, $^1J_{C,F}$ = 270.6 Hz, CF_3), 127.9 (s, 2CH, Ph), 128.0 (s, 2CH, Ph), 128.5 (s, 2CH, Ph), 129.1 (1CH, Ph), 129.4 (1CH, Ph), 129.4 (s, 2CH, Ph), 137.3 (s, 1C, Ph), 140.2 (s, 1C, Ph), 152.5 (q, $^3J_{C,F}$ = 5.6 Hz, $C(Ph)_2$); ^{19}F NMR ($CDCl_3$, 188 MHz): δ –

56.15 (d, $^3J_{H,F}$ = 8.3 Hz, CF_3); IR (KBr): ν = 3085–2851 (=C–H, C–H), 1638, 1575, 1492, 1445, 1366, 1274, 1150–1080 (CF_3), 767, 698, 622 cm^{-1}; ESI-MS: *m/z* 249.2 (100, $[M+H]^+$).

*4.4.2. 2,2,4,4-Tetramethyl-3-(2,2,2-trifluoroethylidene)cyclobutanone (**6d**).* A freshly prepared suspension of Raney-Ni was added to a solution of thiirane **5a** (248 mg, 1.0 mmol) in MeOH (5 ml). The mixture was stirred at room temperature until thiirane **5a** disappeared (TLC control). Then, the mixture was filtered through celite and the solvent was removed under reduced pressure. The resulting oil was purified by standard column chromatography (SiO_2, using mixture of petroleum ether/DCM, in gradient) to give analytically pure **6d**. Yield: 140 mg (68%); colorless oil. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.19 (s, 3H, Me), 1.22 (s, 3H, Me), 1.28 (s, 3H, Me), 1.33 (brs, 3H, Me), 5.40 (q, $^3J_{H,F}$ = 8.8 Hz, 1H, HC(1')); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 20.4 (q, $^5J_{C,F}$ = 2.4 Hz, Me), 21.6 (brd, $^5J_{C,F}$ = 0.9 Hz, Me), 27.0 (q, $^5J_{C,F}$ = 3.0 Hz, Me), 27.3 (brs, Me), 44.8 (s, $C(Me)_2$), 47.0 (brs, $C(Me)_2$), 81.0 (s, C(2')), 109.2 (q, $^2J_{C,F}$ = 35.9 Hz, C(1')), 123.5 (q, $^1J_{C,F}$ = 269.9 Hz, CF_3), 169.7 (q, $^5J_{C,F}$ = 5.4 Hz, C=O); ^{19}F NMR ($CDCl_3$, 188 MHz): δ –58.71 (d, $^3J_{H,F}$ = 8.8 Hz, CF_3); IR (KBr): ν 3023–2830 (=C–H, C–H), 1720 (C=O), 1462, 1346, 1275, 1190, 1172–1073 (CF_3), 1040, 856, 664 cm^{-1}; HRMS (EI): *m/z* calcd. for $C_{10}H_{14}F_3O$ ($[M+H]^+$): 207.2058, found: 207.2068 [100].

*4.5. Synthesis of the trifluoromethyl-1,3-dithiolanes **7** and **8***

A solution of a fluorinated 2,5-dihydro-1,3,4-thiadiazole **3a**,**b** (1.0 mmol) and an appropriate thioketone **2c**,**e**,**f** (1.0 mmol) in toluene (5 ml) was stirred at 100 °C for 24 h. Then, the solvent was removed under reduced pressure and the resulting mixture was purified by standard column chromatography or FLASH column chromatography to give analytically pure compounds.

*4.5.1. 1,1,3,3-Tetramethyl-6,6-diphenyl-7-(trifluoromethyl)-5,8-dithiaspiro[3.4]octan-2-one (**7a**).* Yield: 349 mg (80%); colorless crystals, mp 164–165 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 0.73 (s, 3H, Me), 0.98 (s, 3H, Me), 1.44 (brs, 3H, Me), 1.45 (brs, 3H, Me), 4.75 (q, $^3J_{H,F}$ =7.7 Hz, 1H, C(7)), 7.24–7.29 (m, 4CH, Ph), 7.32–7.35 (m, 2CH, Ph), 7.42–7.43 (m, 2CH, Ph), 7.52–7.53 (m, 2CH, Ph); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 22.8 (s, Me), 22.9 (s, Me), 24.0 (s, Me), 24.3 (s, Me), 61.2 (q, $^2J_{C,F}$ = 26.3 Hz, C(7)), 66.2 (s, $C(Me)_2$), 67.7 (s, $C(Me)_2$), 71.7 (s, spiro-C), 72.6 (s, C(6)), 125.0 (q, $^1J_{C,F}$ = 280.4 Hz, CF_3), 127.2 (s, 2CH, Ph), 127.8 (s, 1CH, Ph), 127.9 (s, 2CH, Ph), 128.0 (s, 2CH, Ph), 128.2 (s, 1CH, Ph), 128.7 (s, 2CH, Ph), 139.6 (s, 1C, Ph), 146.6 (s, 1C, Ph), 219.6 (s, C=O); ^{19}F NMR ($CDCl_3$, 188 MHz): δ –64.35 (d, $^3J_{H,F}$ = 7.7 Hz, CF_3); IR (KBr): ν 3060–2860 (C–H), 1777 (C=O), 1492, 1461, 1359, 1255, 1160–1091 (CF_3), 1033, 935, 699, 609 cm^{-1}; HRMS (EI): *m/z* calcd. for $C_{23}H_{23}F_3OS_2Na$ ($[M+Na]^+$): 459.1040, found: 459.1038 [100].

*4.5.2. 2,2-Dichloro-1,1,3,3-tetramethyl-6,6-diphenyl-7-(trifluoromethyl)-5,8-dithiaspiro[3.4]octane (**7b**).* Yield: 41 mg (9%); colorless oil; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 0.92 (s, 3H, Me), 0.96 (s, 3H, Me), 1.58 (s, 3H, Me), 1.61 (s, 3H, Me), 4.67 (q, $^3J_{H,F}$ =7.8 Hz, 1H, C(7)), 7.25–7.27 (m, 4CH, Ph), 7.32–7.34 (m, 2CH, Ph), 7.39–7.40 (m, 2CH, Ph), 7.48–7.50 (m, 2CH, Ph); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 25.8 (s, Me), 26.6 (s, Me), 27.1 (s, Me), 27.9 (s, Me), 59.1 (s, $C(Me)_2$), 60.1 (s, $C(Me)_2$), 60.7 (q, $^2J_{C,F}$ = 26.4 Hz, C(7)), 72.2 (s, C(6)), 75.1 (s, spiro–C), 99.7 (s, CCl_2), 125.0 (q, $^1J_{C,F}$ = 280.7 Hz, CF_3), 127.0 (s, 2CH, Ph), 127.8 (s, 1CH, Ph), 127.9 (s, 2CH, Ph),

128.0 (s, 1CH, Ph), 128.1 (s, 2CH, Ph), 128.6 (s, 2CH, Ph), 139.4 (s, 1C, Ph), 146.4 (s, 1C, Ph); ^{19}F NMR ($CDCl_3$, 188 MHz): δ – 64.12 (d, $^3J_{H,F}$ = 7.8 Hz, CF_3); IR (KBr): ν 3112–2812, 1494, 1465, 1444, 1384, 1258, 1173, 1192, 1176–1101 (CF_3), 876, 695, 635 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{23}H_{24}ClF_3S_2$ ([M+H–Cl]$^+$): 455.0882, found 455.0883 [100], 457.0856 [55].

*4.5.3. 1,1,3,3-Tetramethyl-6,6-bis(2-thienyl)-7-(trifluoromethyl)-5,8-dithiaspiro[3.4]octan-2-one (**7c**) and 1,1,3,3-tetramethyl-8,8-bis(2-thienyl)-6-(trifluoromethyl)-5,7-dithiaspiro[3.4]octan-2-one (**8c**)* (mixture of regioisomers, ratio 68:32 based on ^{1}H-NMR spectrum). Yield: 309 mg (69%); pale-yellow crystals, mp 84–86 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): major isomer: δ 1.18 (s, 3H, Me), 1.32 (s, 3H, Me), 1.46 (s, 3H, Me), 1.47 (s, 3H, Me), 4.62 (q, $^3J_{H,F}$ =7.8 Hz, 1H, HC(7)); minor isomer: δ 1.28 (s, 3H, Me), 1.70 (s, 3H, Me), 1.72 (s, 3H, Me), one Me signal is not visible, 4.83 (q, $^3J_{H,F}$ =6.5 Hz, 1H, HC(6)); both isomers: δ = 6.86–6.89 (m, 1CH, Thi), 6.96–6.98 (m, 2CH, Thi), 6.99–7.01 (m, 3CH, Thi), 7.26–7.28 (m, 3CH, Thi), 7.30–7.32 (m, 2CH, Thi), 7.36–7.37 (m, 1CH, Thi); ^{13}C NMR ($CDCl_3$, 151 MHz): major isomer: δ 22.2 (s, Me), 23.3 (s, Me), 23.4 (s, Me), 25.1 (s, Me), 64.3 (q, $^2J_{C,F}$ = 26.7 Hz, C(7)), 67.0 (s, $C(Me)_2$), 67.7 (s, $C(Me)_2$), 72.5 (s, C(6)), 124.2 (q, $^1J_{C,F}$ = 281.1 Hz, CF_3), 219.2 (s, C=O); minor isomer: δ 22.4 (s, Me), 23.2 (s, Me), 24.0 (s, Me), 24.2 (s, Me), 48.2 (q, $^2J_{C,F}$ = 31.2 Hz, C(6)), 67.9 (s, $C(Me)_2$), 72.3 (s, $C(Me)_2$), 78.0 (s, C(8)), 125.0 (q, $^1J_{C,F}$ = 278.1 Hz, CF_3), 218.5 (s, C=O); both isomers: δ 125.5 (s, 1CH, Thi), 125.6 (s, 1CH, Thi), 125.8 (s, 2CH, Thi), 126.4 (s, 1CH, Thi), 126.7 (s, 2CH, Thi), 126.8 (s, 1CH, Thi), 127.1 (s, 2CH, Thi), 128.3 (brd, $^6J_{C,F}$ = 0.9 Hz, 2CH, Thi), 142.4 (s, 2C, Thi), 151.7 (s, 2C, Thi); ^{19}F NMR ($CDCl_3$, 188 MHz): major isomer: δ –64.42 (d, $^3J_{H,F}$ = 7.8 Hz, CF_3); minor isomer: δ –67.56 (brs, CF_3); IR (KBr): ν 3288–2494 (C–H), 1695 (C=O), 1572, 1415, 1308–1260 (CF_3), 1142, 1073, 897, 747, 720, 666 cm^{-1}; HRMS (EI): *m/z* calcd. for $C_{15}H_{13}F_3S_4$ ([M-dimethylketene]$^+$): 377.9852, found: 377.9857 [100].

*4.5.4. 1,1,3,3-Tetramethyl-6,6-di(selenophen-2-yl)-7-(trifluoromethyl)-5,8-dithiaspiro[3.4]octan-2-one (**7d**) and 1,1,3,3-tetramethyl-8,8-di(selenophen-2-yl)-6-(trifluoromethyl)-5,7-dithiaspiro[3.4]octan-2-one (**8d**)* (mixture of regioisomers, ratio 66:34 based on ^{1}H-NMR spectrum). Yield: 412 mg (76%); dark-brown solid, mp 108–110 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): major isomer: δ 1.22 (s, 3H, Me), 1.37 (s, 3H, Me), 1.46 (s, 3H, Me), 1.47 (s, 3H, Me), 4.57 (q, $^3J_{H,F}$ =7.8 Hz, 1H, HC(7)); minor isomer: δ 1.29 (s, 3H, Me), 1.70 (s, 3H, Me), 1.72 (s, 3H, Me), one Me signal is not visible, 4.88 (q, $^3J_{H,F}$ =6.4 Hz, 1H, HC(6)); both isomers: δ 7.09–7.10 (m, 1CH, Sel), 7.21–7.25 (m, 3CH, Sel), 7.41–7.42 (m, 3CH, Sel), 7.49–7.50 (m, 1CH, Sel), 7.97–7.98 (m, 1CH, Sel), 8.00–8.02 (m, 2CH, Sel), 8.10–8.12 (m, 1CH, Sel); ^{13}C NMR ($CDCl_3$, 151 MHz): major isomer: δ 64.3 (q, $^2J_{C,F}$ = 26.7 Hz, C(7)), 67.2 (s, $C(Me)_2$), 67.7 (s, $C(Me)_2$), 76.6 (s, C(6)), 124.2 (q, $^1J_{C,F}$ = 281.1 Hz, CF_3), 219.1 (s, C=O); minor isomer: δ 48.7 (q, $^2J_{C,F}$ = 32.7 Hz, C(6)), 71.9 (s, $C(Me)_2$), 72.5 (s, $C(Me)_2$), 78.1 (s, C(8)), 125.0 (q, $^1J_{C,F}$ = 278.1 Hz, CF_3), 218.6 (s, C=O); both isomers: δ 22.1 (brs, 2 Me), 23.3 (brs, 2 Me), 23.4 (brs, 2 Me), 25.4 (brs, Me), one Me signal is not visible, 126.7 (s, 1CH, Sel), 128.3 (s, 1CH, Sel), 129.0 (s, 1CH, Sel), 129.5 (s, 1CH, Sel), 130.5 (brs, 2CH, Sel), 131.6 (brd, $^6J_{C,F}$ = 1.9 Hz, 3CH, Sel), 133.2 (brd, $^5J_{C,F}$ = 3.6 Hz, 3CH, Sel), 149.5 (s, 2C, Sel), 160.9 (s, 2C, Sel); ^{19}F NMR ($CDCl_3$, 188 MHz): major isomer: δ –63.80 (d, $^3J_{H,F}$ = 7.8 Hz, CF_3); minor isomer: δ –67.45 (d, $^3J_{H,F}$ = 6.4 Hz, CF_3); IR (KBr): ν 3109–2830 (C–H), 1776 (C=O), 1460, 1440, 1255, 1173,

1180, 1165–1090 (CF_3), 729, 692, 659 cm^{-1}; HRMS (EI): *m/z* calcd. for $C_{15}H_{13}F_3S_2Se_2$ ([M-dimethylketene]$^+$): 473.8741, found: 473.8742 [100], 471.8764 [90], 469.8776 [50], 475.8744 [40], 467.8794 [30].

*4.6. Synthesis of the trifluoromethyl-substituted alkenes **6b**,**c** and 4,4,5,5-tetrasubstituted 1,3-dithiolanes **9a**,**b***

To a mixture of DCM/H_2O (10 ml, v/v: 10:1), a thioketone **2e**,**f** (1.0 mmol), sodium nitrite (207 mg, 3.0 mmol), and solid 2,2,2-trifluoroethylamine hydrochloride (271 mg, 2.0 mmol) were added at room temperature under Ar atmosphere. The mixture was vigorously stirred at this temperature until the color of the starting thioketone disappeared. The mixture was left at room temperature overnight. Then, water (15 ml) was added and the products were extracted using DCM (3x10 ml). The organic layers were combined, dried over anhydrous Na_2SO_4, and the solvent was removed *in vacuo*. The resulting oil was purified by standard column chromatography or FLASH column chromatography to give analytically pure products.

*4.6.1. 3,3,3-Trifluoro-1,1-bis(2-thienyl)prop-1-ene (**6b**).* Yield: 159 mg (61%); grey oil; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 6.21 (q, $^3J_{H,F}$ = 8.2 Hz, 1H, HC(2)), 7.03–7.04 (m, 1CH, Thi), 7.07–7.08 (m, 1CH, Thi), 7.11–7.13 (m, 1CH, Thi), 7.24–7.25 (m, 1CH, Thi), 7.39–7.40 (m, 1CH, Thi), 7.49–7.51 (m, 1CH, Thi); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 114.9 (q, $^2J_{C,F}$ = 34.5 Hz, C(2)), 122.8 (q, $^1J_{C,F}$ = 270.1 Hz, CF_3), 126.7 (s, 1CH, Thi), 127.7 (s, 1CH, Thi), 127.8 (s, 1CH, Thi), 128.0 (s, 1CH, Thi), 128.4 (s, 1CH, Thi), 129.6 (brd, $^5J_{C,F}$ = 2.1 Hz, 1CH, Thi), 136.0 (s, 1C, Thi), 138.8 (q, $^3J_{C,F}$ = 5.8 Hz, $CThi_2$), 143.6 (s, 1C, Thi); ^{19}F NMR ($CDCl_3$, 188 MHz): δ –64.15 (d, $^3J_{H,F}$ = 8.2 Hz, CF_3); IR (KBr): ν 2988–2830 (=C–H, C–H), 1620, 1431, 1270, 1181–1093 (CF_3), 857, 700 cm^{-1}; HRMS (EI): *m/z* calcd. for $C_{11}H_7F_3S_2$ ([M]$^+$): 260.3010, found: 260.3016 [100].

*4.6.2. 3,3,3-Trifluoro-1,1-di(selenophen-2-yl)prop-1-ene (**6c**).* Yield: 170 mg (48%); grey oil; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 6.13 (q, $^3J_{H,F}$ = 8.1 Hz, 1H, HC(2)), 7.26–7.28 (m, 1CH, Sel), 7.33–7.35 (m, 2CH, Sel), 7.39–7.40 (m, 1CH, Sel), 8.07–8.08 (m, 1CH, Sel), 8.21–8.22 (m, 1CH, Sel); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 114.6 (q, $^2J_{C,F}$ = 34.3 Hz, C(2)), 122.8 (q, $^1J_{C,F}$ = 270.3 Hz, CF_3), 128.9 (s, 1CH, Sel), 130.3 (s, 1CH, Sel), 131.6 (s, 1CH, Sel), 131.7 (brd, $^5J_{C,F}$ = 2.0 Hz, 1CH, Sel), 133.6 (s, 1CH, Sel), 133.7 (s, 1CH, Sel), 141.9 (s, 1C, Sel), 142.9 (q, $^3J_{C,F}$ = 5.5 Hz, $CSel_2$), 149.9 (s, 1C, Sel); ^{19}F NMR ($CDCl_3$, 188 MHz): δ –64.69 (d, $^3J_{H,F}$ = 8.1 Hz, CF_3); IR (KBr): ν 2993–2827 (=C–H, C–H), 1619, 1460, 1360, 1266, 1187–1089 (CF_3), 881, 770, 689 cm^{-1}; HRMS (EI): *m/z* calcd. for $C_{11}H_7F_3Se_2$ ([M]$^+$): 355.8830, found: 355.8833 [100], 353.8842 [90], 351.8853 [55], 357.8832 [30], 349.8869 [25].

*4.6.3. 4,4,5,5-Tetrakis(2-thienyl)-2-(trifluoromethyl)-1,3-dithiolane (**9a**).* Yield: 181 mg (36%); light–brown solid, mp 122–124 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.14 (q, $^3J_{H,F}$ =6.8 Hz, 1H, HC(2)), 6.92–6.94 (m, 4CH, Thi), 7.09–7.10 (m, 1CH, Thi), 7.15–7.16 (m, 2CH, Thi), 7.26–7.28 (m, 2CH, Thi), 7.30–7.31 (m, 2CH, Thi); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 50.5 (q, $^2J_{C,F}$ = 33.0 Hz, C(2)), 74.7 (s, C(4), C(5)), 124.9 (q, $^1J_{C,F}$ = 279.0 Hz, CF_3), 125.8 (s, 2CH, Thi), 125.9 (s, 2CH, Thi), 127.0 (s, 2CH, Thi), 127.5 (s, 2CH, Thi), 130.2 (s, 2CH, Thi), 131.3 (s, 2CH, Thi), 145.6 (s, 4C, Thi); ^{19}F NMR ($CDCl_3$, 188 MHz): δ –65.71 (d, $^3J_{H,F}$ = 6.8 Hz, CF_3); IR (KBr): ν 3126–2833 (C–H), 1622, 1420, 1316, 1281, 1200, 1180–1111 (CF_3), 816, 726, 682, 652 cm^{-1}; HRMS (EI): *m/z* calcd. for $C_{20}H_{14}F_3S_6$ ([M+H]$^+$): 503.7030, found: 503.7039 [100].

*4.6.4. 4,4,5,5-Tetra(selenophen-2-yl)-2-(trifluoromethyl)-1,3-dithiolane (**9b**).* Yield: 248 mg (36%); light–brown solid, mp 132–134 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.16 (q, $^{3}J_{H,F}$ =7.1 Hz, 1H, HC(2)), 7.19–7.21 (m, 4CH, Sel), 7.46–7.48 (m, 4CH, Sel), 8.03–8.06 (m, 4CH, Sel); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 50.8 (q, $^{2}J_{C,F}$ = 32.9 Hz, C(2)), 78.3 (s, C(4), C(5)), 124.8 (q, $^{1}J_{C,F}$ = 279.1 Hz, CF_3), 128.3 (s, 2CH, Sel), 128.4 (s, 2CH, Sel), 133.0 (s, 2CH, Sel), 134.1 (s, 2CH, Sel), 134.4 (s, 2CH, Sel), 134.7 (s, 2CH, Sel), 151.6 (s, 4C, Sel); ^{19}F NMR ($CDCl_3$, 188 MHz): δ –65.40 (d, $^{3}J_{H,F}$ = 7.1 Hz, CF_3); IR (KBr): ν 3122–2830 (CH), 1420, 1310, 1285–1194 (CF_3), 1180, 1144, 1111, 833, 700, 659 cm^{-1}; HRMS (EI): *m*/*z* calcd. for $C_{20}H_{13}F_3S_2Se_4$ ($[M]^+$): 693.7072, found: 693.7048 [90], 691.7052 [100], 689.7070 [95], 687.7097 [80], 685.7106 [60], 695.7019 [60].

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